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I, JONNE YABSLEY, TEAM LEADER EXAMINATION SUPPORT AND
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in connection with Application No. 2002953252 for a patent by HUNTSMAN
CORPORATION AUSTRALIA PTY LTD as filed on 09 December 2002.



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J R Yabsley

JONNE YABSLEY
TEAM LEADER EXAMINATION
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Huntsman Corporation Australia Pty Ltd
(A.C.N. 083 984 187)

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PROVISIONAL SPECIFICATION
 for the invention entitled:

"Composition, Compounds and Methods for their Preparation"

The invention is described in the following statement:

COMPOSITIONS, COMPOUNDS AND METHODS FOR THEIR PREPARATION

Field of the Invention

The invention relates to novel compounds, compositions and methods for their preparation. The compounds and compositions of the present invention find particular application as foaming or frothing agents in ore and coal flotation processes. The compounds and compositions may also find applicability as surfactants in hydraulic fluids.

Background of the Invention

Froth flotation is a widely used process for separating fine solids from other solids by taking advantage of the disparity in wettability at solid particle-surfaces. Separation of a solid mixture may be accomplished by the selective attachment of hydrophobic solid particles to gas bubbles. Most often the gas used is air, which is generally passed through a liquid mixture of the crude solids at such a rate as to provide a sustained "froth" or accumulation of bubbles at the liquid-surface interface. The density difference between the gas bubbles and liquid provides the attached solid particles with buoyancy, lifting the hydrophobic solid particles to the surface and leaving behind non-hydrophobic solids in the bulk liquid mixture. The hydrophobic solid particles at the surface remain attached to the surface froth and can be subsequently separated from the bulk mixture by draining the bulk mixture or mechanically skimming the surface froth.

In froth flotation a frothing or foaming agent is added to stabilise the bubbles which carry the hydrophobic solid particles to the surface. The stabilization of the bubbles or surface froth, greatly enhances the separating efficiency of the unwetted hydrophobic particles from the bulk liquid-solid mixture. The frothing agent or "frother" acts by stabilizing the bubbles through the lowering of the liquid surface tension enhancing the performance of dissolved air froth flotation processes.

Froth flotation techniques have been used in the mining industry for around 150 years. Many different minerals including, silver, nickel, zinc, titanium, cobalt, and chromium are processed using froth flotation. Today, mining companies are finding it more and more difficult to find high grades of ore. Accordingly, there is a growing demand to provide more

effective mineral separation processes to balance the ever increasing economical burden which mining companies face as they process poorer grades of ore. As such, improvements in froth flotation techniques would be of much benefit to the present day mining industry.

5 Froth flotation has also been used in other industries including the chemical industry. It is also used in sewage and water treatment, paper de-inking and so on. A major user of froth flotation is the coal industry for desulfurization and for the recovery of "clean coal". Clean coal is required by end users who set defined specifications for the coal that they purchase. These will usually include maximum limits on ash or "non combustible" matter in the form of clays, 10 gypsum and other minerals, as well as the maximum sulphur content in order to minimise discharge of environmentally unfriendly SO_x gases upon combustion of the coal.

Processes for floating coal or minerals can be carried out in specially designed flotation devices such as a Jameson Cell, Microcel or other column cells.

15

A good frother must possess a number of key properties. Different frothers will be better suited to different applications, however, in general terms, a frother must be able to promote the formation of stable air bubbles under aerated conditions. Frothers are typically comprised of both polar and non polar components. The non polar or hydrophobic moiety will orient itself 20 into the air phase while the polar or hydrophilic component will tend to the liquid (usually water) phase. The result is an enhanced bubble wall strength and stability due to localised increase in surface tension. This will enhance the ability of the bubbles to hold and concentrate the desired mineral.

25 Effective frothers usually contain at least 5 carbon atoms in a straight chain or branched configuration which provide the hydrophobic interaction with the air phase and a polar group which is typically a hydroxyl (-OH) functionality. The balance of these two functionalities will determine the effectiveness of a particular frother for a particular application. Typical frothers currently in use in the mining industry include aliphatic alcohols like 2-ethyl-3-hexanol, cyclic 30 alcohols (for example, pine oil), 1,1,3 - triethoxybutane, and polyalkylene glycols.

One of the most commonly used all purpose flotation frothers for coal, base metal and

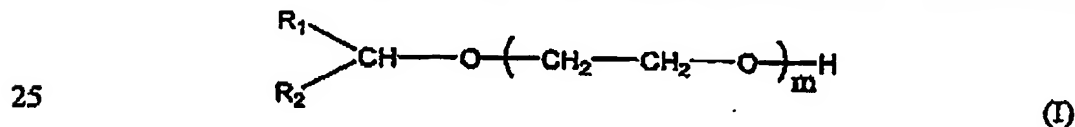
other non-metal flotation is 4-methyl-2-pentanol, commonly known as "MIBC" (methyl isobutylcarbinol).

MIBC displays excellent surface behaviour, solubility and has been widely adopted in the industry due to its relatively low cost and good froth generation performance, especially in applications where the minerals are relatively hydrophobic and readily floatable. However, MIBC is highly flammable displaying a Pensky-Martens and closed cup flash point of 41°C (106°F). MIBC also omits an unpleasant odour and accordingly is not very pleasant to work with. MIBC is classified as a dangerous good according to the National Standard for the Storage and Handling of Workplace Dangerous Goods [NOHSC; 1015(2001)] and the National Code of Practice: Storage and Handling of Workplace Dangerous Goods [NOHSC: 2017(2001)] and accordingly, requires special care when handled, transported or stored in large volumes. Consequently, this compound poses a substantial occupational, health and safety (OH&S) concern. It is apparent from this that a need exists for a less volatile alternative to MIBC, that has better flammability and odour characteristics and is generally safer to deal with in general use.

Summary of the Invention

It has now been surprisingly found that C₃-C₉ secondary alcohols having a low degree of ethoxylation have the ability to act as effective frothers, and also have the added advantage of possessing higher flash points over the parent alcohols, making them less flammable and less volatile. These compounds also display better odour characteristics than the parent alcohols.

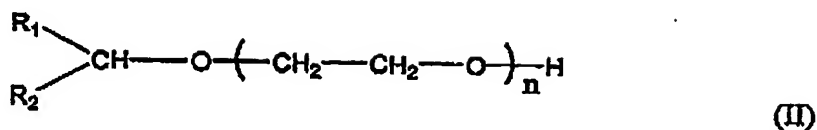
Accordingly, in one aspect the present invention provides compounds of the formula (I):



wherein R₁ and R₂ are each independently C₁-C₄ alkyl, and m is 1, 2, 3, 4, or 5.

In another aspect the invention provides a composition comprising at least two compounds of the formula (II):

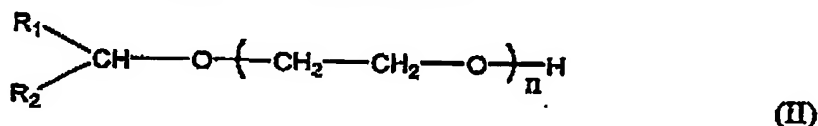
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wherein R_1 and R_2 are each independently C_1 - C_4 alkyl, and n is an integer ≥ 0 and wherein the average molar value of n for the total of the compounds of formula (II) in said composition is in the range of 1 to 3.

5

In yet another aspect, the present invention provides a method for preparing a composition comprising at least two compounds of formula (II):



wherein R_1 and R_2 are each independently C_1 - C_4 alkyl, and n is an integer ≥ 0 , and

10 wherein the average molar value of n for the total of the compounds of formula (II) in said composition is in the range of 1 to 3, said method comprising:

reacting an excess of C_3 - C_9 secondary alcohol with ethylene oxide in the presence of a catalyst in an ethoxylation vessel to form a mixture of two or more compounds of formula (II),

15 separating at least a portion of unreacted secondary alcohol from the mixture, and recycling unreacted secondary alcohol back into the ethoxylation vessel.

The term C_1 - C_4 alkyl group refers to straight chain or branched alkyl groups of from 1 to 4 carbon atoms. Examples of suitable alkyl groups include methyl, ethyl, n-propyl, 20 cyclopropyl, isopropyl, n-butyl, iso-butyl, tert-butyl and cyclobutyl. Preferably the group R_1R_2CH- is selected from the group consisting of pent-4-yl, pent-2-yl, pent-3-yl, 2-methyl-pent-3-yl, 4-methyl-pent-2-yl, hex-2-yl, hex-3-yl.

Most preferably the group R_1R_2CH- is 4-methyl-pent-2-yl.

25

The R_1R_2CH- group together with the O atom in the compounds of formula (I) can be derived from a C_3 - C_9 secondary alcohol. Accordingly, the group R_1R_2CHO- represents the residue of a C_3 - C_9 secondary alcohol. As such, the compound of formula (I) according to the present invention may be prepared by ethoxylating a secondary alcohol with ethylene oxide

(EO). It will be recognised that m in formula (I) refers to the number of molecules of EO which have added per molecule of the secondary parent alcohol.

It will be understood that R_1 and R_2 may independently represent different C_1 - C_4 alkyl groups or the same C_1 - C_4 alkyl group.

The most preferred compounds of the present invention are those in which m is 1-5. More preferable are those compounds in which m is 1-3.

Preferable compounds of formula (I) are those which exhibit a closed cup flash point of greater than or equal to 61°C . Most preferred compounds of formula (I) are those which exhibit a closed cup flash point of greater than 65°C . In the description which follows (including the examples) the quoted flash points of the compounds and compositions of the present invention are measured using a Pensky-Marten flashpoint apparatus, however for the purposes of the present invention it has been found that the determination of the flash point using the Pensky-Marten method is directly comparable to the closed cup method.

Primary alcohols generally react much faster than secondary alcohols during ethoxylation with EO. Because of the disparity in reaction rates between primary and secondary alcohols there is a tendency for EO to react with secondary alcohols which have already been ethoxylated, than to react with a molecule of an unreacted parent secondary alcohol. Accordingly, the product mixtures of such reactions will invariably contain mixtures of ethoxylated, multi-ethoxylated and non-ethoxylated secondary alcohols. Surprisingly, it has now been found that compositions of such mixed products comprising at least two compounds of formula (II) are also effective frothing agents.

With specific reference to the compositions of the parent invention the term "average molar value of n " refers to the combined molar average of ethoxylated compounds of formula (II) which are present in the compositions of the present invention. For the present invention the average molar value of n is in the range of 1 to 3, and more preferably 1 to 2 and most preferably about 1.7.

It will be understood that n refers to the number of ethylene oxide molecules which have been substituted per molecule of C_3 - C_9 secondary alcohol. In the present invention n is an integer greater than or equal to 0. As such, the compositions of the present invention may comprise non-ethoxylated products ($n=0$), mono-ethoxylated products ($n=1$) and multi-ethoxylated products ($n>1$). Therefore, the compositions of the present invention will be understood to comprise a mixture of mono-ethoxylated and non-ethoxylated products, mono-ethoxylated and multi-ethoxylated products, multi-ethoxylated and non-ethoxylated products or a combination of mono, non, and multi-ethoxylated products, wherein the average molar value of n of the composition is in the range of 1 to 3.

It is generally thought that ethoxylation of alcohols will greatly alter their properties in relation to those of the parent alcohol. Unexpectedly, it has been found that the compositions of the present invention display surface behaviour which is very similar to that of the parent alcohol. The additional advantage of the compounds and compositions of the present invention is that their flash point is raised relative to the parent alcohol without losing the characteristics which make for a good frother.

The flash points of the compositions of the present invention can be controlled to a desired level by varying the amount of $n=1$ (monoethoxylate product), and/or $n=0$ (parent alcohol or non-ethoxylated product) in the composition. Although maintaining good frothing qualities these compounds ($n=1$, or 0) tend to have lower flash points with respect to the same compounds which have undergone multiple ethoxylation (ie., where $n>1$). As a result, the compositions of the present invention display the same properties which the parent alcohol displays including the formation of a dry brittle and effervescent froth, and similar froth stability. However, the composition of the present invention are superior frothers in comparison with the parent C_3 to C_9 alcohols as they have the added advantage of higher flash points, and accordingly are less volatile.

The compositions of the present invention may have an amount of unreacted parent C_3 - C_9 secondary alcohol (ie, where n is 0) that is less than 15% by weight of the total composition. It is preferred that the composition contain no more than 10% of the parent alcohol. More preferably however, the compositions of the present invention contain no more than 8% of the

It is also a preferred feature that the compounds of formula (II) wherein n is greater than 4 account for less than 20% by weight of the total composition.

The present invention has been developed for the purposes described herein. The composition may be blended with a number of other products in its final use dependant on the requirements of the application. These include but are not limited to other frothers (eg alcohol or glycol type), collectors (eg kerosene), dispersants, depressants, water or other solvents.

The method for obtaining the desired compositions can be achieved through restricting the degree of ethoxylation of the secondary alcohol and then removing the compounds where ($n=0$ and/or $n=1$) from the composition mixture in a single distillation. A person skilled in the art would understand that the degree to which ethoxylation of the compounds of formula (I) can be restricted will be dependent upon the catalyst and reaction conditions used. Primarily, a lower degree of ethoxylation can be achieved by reacting an amount of secondary alcohol which is in a molar excess with respect to the amount of EO. Preferably the ratio of EO to secondary alcohol is kept below 70 wt%. More preferably the ratio is below 12%. In this manner the excess parent alcohol can be distilled, recycled, or reused in a further process.

It will be understood that the compounds of formula (I) of the present invention are also preferably prepared by the same methods which are used to prepared the composition of the present invention. Accordingly, the present invention provides for subsequent distillation of the compounds of formula (I) where $m = 1, 2, 3, 4$, or 5 . Distillation techniques for separating closely boiling fractions, either by atmospheric or reduced pressure techniques, including spinning band distillation and fractional distillation, can be used in isolating the compounds of formula (I). Other techniques for isolating compounds of formula (I) would be known to those skilled in the art.

According to the present invention, the levels of compounds where $n=0$ and/or $n=1$ in the final composition can be varied by distillation techniques to achieve the desired flash point. For instance, the present invention allows for variation in the amount of the parent secondary

alcohol to adjust the flash point of the composition to a desired level. As such the flammability or flash point of the compositions can be varied depending largely on the remaining amount of parent alcohol ($n=0$) left in the composition. In a preferred embodiment, the flash point of the composition is greater than or equal to 61 °C (as measured by the closed cup method defined in AS/NZS 2106.2) so as to allow classification of the composition as non flammable according to the definition of a flammable liquid described in the Australian Dangerous Goods Code. Through varying the level of the parent alcohol remaining in the compositions of the present invention one will be able to also vary the flash point to suit the storage, transport or use requirements for the compositions. Alternatively, as the compounds and compositions of the present invention are likely to be miscible with water, then one skilled in the art would understand that water could also be added to increase the flash point and therefore decrease flammability. For instance it has been found that the addition of about 10% wt of water to the composition of the present invention renders it essentially non-flammable below 100°C.

In the manufacture of the compounds and compositions of ethoxylates of the present invention, the reaction is facilitated by addition of acid or base catalyst.

Preferably, the base catalyst is derived from alkali and alkaline earth metals. Most preferably, the best catalyst is an alkaline metal hydroxide such as lithium, sodium or potassium. The most preferred is potassium hydroxide.

The ethoxylation process of the present invention may also be catalysed with the use of Lewis acids (for example, boron trifluoride, antimony pentachloride, tin (IV) chloride, or aluminium alkylates) or Bronsted acids (for example, p-toluene sulphonic acid, fluorosulfonic acid or perchloric acid). The most preferred Lewis acid is boron trifluoride used as the etherate, or as a complex preformed with the alcohol.

The most preferred base catalyst for preparing the compounds and compositions of the present invention is potassium hydroxide, with the most preferred catalyst being potassium hydroxide which has been dissolved in MIBC and dehydrated. Of the acid catalysts, boron trifluoride is the most preferred due to its ease of handling, availability and high rates of reaction. Narrow range ethoxylation catalysts (NRE's) are also a preferred group of catalysts

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that are neither acid nor base catalysts, but give a narrow molecular weight range of products.

The reaction may be done in a single pot or a two step process. In a two step process, the base catalyst is added to the alcohol to initially prepare an alkoxide ion. Accordingly, when
5 the catalyst is potassium hydroxide and the secondary alcohol is MICB, the alkoxide ion is potassium 4-methyl-2-pentoxide. It will be appreciated that water produced as a by-product from this initial reaction can be distilled off (removed) prior to the addition of EO.

In another embodiment, the EO may initially be reacted with an acid catalyst which
10 activates EO to nucleophilic attack.

It is emphasized however that the preferred method for preparing the compositions and compounds of the present invention is performed in a single pot or in a continuous process. The most preferred method for preparing the compositions and compounds of the present
15 invention is a continuous process. In a continuous operation, a small amount of EO is added to catalysed MIBC and reacted out. The product is then distilled to recover most of the unreacted MIBC, which is then recycled. The product is then collected *as is*, or is further distilled to recover the product and leave a residue containing catalyst, PEG's and highly built MIBC ethoxylates. Continuous plant processes suitable for carrying out this are known, and are
20 commercially available. A typical version comprises a long heated pipe in which the alcohol flows as it is being reacted. To save space, such reactors are often bent back on themselves in a series of S's, and are often referred to as Serpentine reactors.

The compounds and compositions of the present invention can be used as a frothing
25 agent in existing froth flotation processes. They can be used as replacements for existing frothers or to supplement frothers currently used. An example of how the present composition and compounds of the present invention can be used as a frother in a typical mineral or coal flotation plant process is as follows:

30 1. The frother is typically added to either a conditioning vessel prior to flotation or to the first flotation cell directly, depending on the amount of time and agitation required to disperse the product in the mineral/coal slurry. In the case of Jameson cells the frother is added to the

downcomer portion of the cell to optimise dispersion within the high shear environment typical of this type of cell. Other reagents such as collectors and dispersants may be added at the same time.

- 5 2. Once in the flotation cells the frother acts to facilitate the generation of a stabilised froth to aid in the recovery of fine particles. The desired mineral or coal particles are concentrated through attachment of these particles to the stable air bubbles which rise to the top of the cell. Other reagents at this point will assist with selective collection of the desired minerals, and depression of unwanted gangues or other minerals.

10

3. The mineral/coal enriched froth concentrate is then collected from the top of the cell either passively by over spilling into collection launders or by mechanical skimming.

4. The mineral/coal enriched concentrate may then be subjected to further flotation
15 cleaning to further enhance the selectivity of desired mineral/coal. Further flotation may or may not require additional frother dosing.

5. The final concentrate is typically collected and thickened/dried before further processing.

20

It will be appreciated that although the preferred use of the present invention is as a frother in mineral flotation, the compounds and compositions thereof may also be applicable to other uses which currently utilises C₃-C₉ alcohols. For instance, the ethoxylated products of the present invention may find use as surfactants in hydraulic fluids. The products may be used to
25 create water-in-oil and/or oil-in-water emulsions which may then be used as fire-resistant hydraulic fluids. The surface active nature and molecular structure of the product is such that it may assist in the formation of micelles to provide emulsion stability and other desirable properties, along with the use of other chemicals as dictated by design requirements.

30

Examples

Examples 1

MIBC was charged to an autoclave with potassium hydroxide (KOH) as catalyst.

- 5 The charge was heated to 160 °C under stirring and ethylene oxide added slowly. Reaction progress was monitored by observing the rise and fall in pressure as EO was added and reacted, and the rise in temperature due to reaction. If the absolute pressure rose above 200 kPa, EO addition was stopped until it fell below 200 kPa again.

- 10 Product was fractionally distilled to selectively remove all of the free, unreacted MIBC. Distillation was carried out at atmospheric pressure where the boiling point of MIBC is 132 °C. A controlled amount of fresh MIBC was then added back.

- 15 Product was analyzed by gas chromatography as made, and then again after distillation and after addition of the free MIBC. Pensky-Martens Closed Cup flash point was measured by standard methods. The froth properties of the products were assessed by two phase flotation tests in a 2 litre laboratory Agitair flotation cell. The main observations made were froth structure and stability and volume of froth generated under standard conditions. These were compared to results using MIBC.

20

The product was not neutralized, and was a light teak colour due to the decomposition of minor impurities (<1% by mass) in the feed material.

Detailed conditions and results for four runs are given below in Table 1.

TABLE I

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Example 2

MIBC was charged to an autoclave and Boron Trifluoride Etherate $\text{BF}_3 \cdot \text{OEt}_2$ added as catalyst. The charge was heated to 100°C under stirring and EO added and reacted. Due to the
5 different selectivity of the BF_3 catalyst, a far higher ratio of EO could be added to the alcohol, but excess alcohol still needed to be removed by distillation.

The product was distilled under vacuum (water pump vacuum, ~ 15 mm Hg) in a rotary
film evaporator at 90°C . Under these conditions some of the MIBC mono-ethoxylate is
10 removed along with the free MIBC, but the residual free MIBC can be controlled by the distillation temperature.

The product was analyzed for Pensky-Martens Closed Cup flash point, and for
composition by gas chromatography. Laboratory froth performance was also assessed as
15 before.

Detailed conditions and results for two runs are given below in Table 2.

TABLE 2

Run:	1	2
Catalyst	BF ₃	BF ₃
Loading	2,300	2,300
EO/Kg	540	540
	vacuum distilled	
MIBC +		
0 EO	7.32	5.28
1 EO	28.93	29.43
2 EO	28.45	29.31
3 EO	18.25	18.69
4 EO	9.24	9.45
5 EO	3.80	3.88
6 EO	1.35	1.34
7 EO	0.41	0.40
8 EO	0.08	0.00
9 EO	0.00	0.00
10 EO	0.00	0.00
Other ¹		
Br ²	1.74	1.81
ratio ³		
n>4 ⁴	5.6%	5.6%
Flash Pt ⁵	71°C	74°C
Notes:	<ol style="list-style-type: none"> 1. Other. Unidentified peaks, including Poly Ethylene Glycols (PEG's). 2. BR=Build Ratio. Total moles of EO in MIBC ethoxylates over total moles of MIBC as free alcohol and as ethoxylates. 3. ratio=A measure of tailing of the product distribution, calculated as $(M3+M4)/(M1+M2)$, where Mn is the wt% of the MIBC ethoxylate with n EO residues. 4. n>4. A measure of tailing of the product distribution, calculated as the total wt% of all MIBC ethoxylate with more than 4 EO residues as a fraction of all MIBC and MIBC ethoxylate species present. 5. Flash Pt. Pensky-Martens Closed Cup flash point as measured by standard methods. 	

5 This product was submitted for preliminary screening as a frother in coal washing, and in sulphide mineral flotation. Results suggest that the product is at least comparable to MIBC in flotation performance.

10 Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

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Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within the spirit and scope. The invention also includes all of the steps, features, compositions and compounds
5 referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

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